BIO-RESOURCE DERIVED NATURAL PIGMENTS FOR HETEROSTRUCTURED- SEMICONDUCTOR BASED PHOTOCATALYSIS: WASTE WATER REMEDIATION

A Synopsis

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Introduction

Rapid development of industrialization has been extensively polluted the ecosystem by the disposal of waste water [1, 2]. Many heavy metals, inorganic and organic waste when released into the aquatic environment are recognized to be poisonous, carcinogenic and causes various diseases and disorders in human, animals and aquatic life [3]. The noxious pollutants in the marine environment is mainly due to the discharge of industrial sewage of textile, pharmaceutical, battery manufacturing etc. [4]. Many techniques has been implemented for the elimination of inorganic and organic impurities from the wastewater. These techniques includes adsorption [5], activated sludge treatment [6], precipitation [7], evaporation [8], reverse osmosis [9], ultrafiltration [10], microfiltration [11], solid-liquid separation [12], ion-exchange [13], coagulation [14] etc. But these approaches have been found lesser effective in the removal or mineralization of emergent organic pollutants. So more effective routes have been required for the emission of emergent hazardous pollutants [15]. Presently, Advanced Oxidation Processes (AOPs) has been attaining great consideration for elimination of the noxious pollutants [16]. AOPs can be categorized into two groups:

a) Non-photochemical AOPs which contain Fenton and Fenton-like processes, cavitation and ozonation [17-19].

b) Photochemical AOPs which contain heterogeneous and homogeneous photocatalysis [20, 21].

The formation of highly active hydroxyl radicals (HO•) (in AOPs) is the significant step for efficient removal and mineralization of inorganic and organic contaminants in water [22, 23]. Among these, heterogeneous photocatalysis has been demonstrated an effective process for high degradation, eco-friendly, cost effective, non-toxic, low temperature and pressure conditions and easily operated [24, 25]. For the elimination of noxious contaminants, the major hindrance is deficiency of ideal semiconductors photocatalysts. The perfect photocatalyst generally have an appropriate band gap, high charge carrier's mobility and long-lived electrons-holes separation, high absorption coefficient for proficiently harvesting solar light [26]. Therefore, numerous methodologies have been tried to fabricate efficient photocatalyst by either doping including metal or non-metal, sensitization, morphology control, heterojunction built metal [27, 28]. Now days, researchers have attained more interest in fabrication of hetero-structure semiconductor due to greater photocatalytic performances as compared with single semiconductor [29]. The photo-induced electrons and holes proficiently transfer from one semiconductor to coupled semiconductor and retards the electron-hole recombination in the

photocatalytic action [30]. In recent times, researchers are found to be more fascinated in the fabrication of carbonaceous based binary or ternary composite, just to bring a synergistic effect. The carbon based materials such as graphene oxide, reduced graphene oxide, activated carbon etc. plays an efficient role in the photocatalysis due to outstanding electronic and thermal properties, high specific surface area, mechanical and optical characteristics [31, 32]. Carbon based materials act as a supportive material to provide sufficient active sites for aggregation of various substrates and retards the recombination of photogenerated electron-hole pairs [33]. Carbonaceous materials are nontoxic, eco-friendly and easy available in the ecosystem. Natural dyes have been widely used as a sensitizer because synthetic dyes having weak binding energy with semiconductors. Sensitizer adsorbs on the upper most layer of semiconductor and excited electrons of sensitizer moves from VB to CB of semiconductor by the absorption of photon, which facilitate electron mobility into semiconductor [34, 35]. Natural dyes can be drawing out or extracted from flowers, fruits, leaves, tree barks, roots etc. Various natural dyes for example beta lain, chlorophyll, carotenoid, anthocyanin, flavonoid, cyanine, and tannin etc. are easily accessible, easily extracted, cost effective, non-toxic, eco-friendly and completely biodegradable [36, 37]. The solvent have vital role in the extraction of natural dyes. Various kinds of organic solvents have been utilized for natural dyes extraction from the plants. The nature of solvent affects the binding between dyes and semiconductors and also the absorption spectrum [38].

Literature Review

The industrial development is essential for the economic evolution. However, the discharge of various contaminants with or without treatments are hazardous to the ecosystem specifically dyes and dyes-based toxic wastewater sewages. Dyes are utilized in numerous industries including cosmetic, pharmaceutical, tannery, food, photographic, paper and pulp and plastic industries. These chemicals are excluded in the main water resources which have carcinogenic and mutagenic nature and also vanishing the equilibrium of the ecosystem. Thus, unsustainable waste disposal required an efficient cost-effective, environment friendly, easily operative techniques [39].

Nowadays, photocatalysis is an advanced oxidation process (AOPs) considered as an inexpensive and having wide range of environmental applications. In 1972, Fujishima and Honda were firstly used Pt-attached n-TiO_2 for photo electrochemical (PEC) H_2 production from water splitting. Afterwards, Bard extended the proposition of photo electrochemical water splitting system to the heterogeneous photocatalytic systems by using semiconductor particles

suspended in water as photocatalyst. Subsequently, the heterogeneous photocatalysis has been broadly used as water splitting, environmental remediation, CO_2 reduction, disinfection and selective organic transformations. Modern developments have been demonstrated that hetero-structured semiconductors nanocomposites can be proposed as the most promising novel catalysts in the photocatalytic degradation of industrial wastes [40].

Gomez-Ruiz et al., (2018) investigated the degradation of perfluorooctanoic acid by the use of TiO_2/RGO which is fabricated via hydrothermal method. The photocatalyst TiO_2-RGO (0.1 g L^{-1}) dispersed in PFOA (0.24 mmol L^{-1}). Under 12 h of UV-vis irradiation, degradation of PFOA reached to 93% [41].

Zhu et al., (2017) studied the photocatalytic degradation of sulfamethoxazole (SMX). The RGO-WO_3 nanostructure was synthesized via facile one step hydrothermal process. About 98% SMX degradation attained under 3 hours visible light irradiation [42].

Ding et al., (2015) prepared molybdenum disulfide-graphene oxide (MoS_2-GO) composite hydrogel by a one-step hydrothermal scheme. MoS_2-GO photocatalyst showed insuperable exclusion of methylene blue (MB). The MoS_2-GO nanocomposite degrade 99% of MB after 60 min under solar lights irradiation [43].

Begum et al., (2018) synthesized SnO_2/Activated carbon (SnO_2/AC) photocatalyst nanocomposite by hydrothermal method. SnO_2/AC nanocomposite showed an insuperable photocatalytic property as compared to pure SnO_2 for degradation of Naproxen. About 30 mg of photocatalyst was dispersed within 50 ml of 5 mgl^{-1} Naproxen and irradiated under direct sunlight for 2 h. At pH 3, the photocatalyst degraded 94% of Naproxen solution in 2 h. The synergistic effect of SnO_2 and AC have high rate constant which creates the SnO_2/AC nanocomposite as an excellent photocatalyst [44].

Zhu et al., (2017) synthesized silver carbonate (Ag_2CO_3) loaded activated carbon (AC) composite by ion-exchange deposition method. As compared with pure Ag_2 CO_3, the Ag_2 CO_3/AC composite have larger surface area and high photodegradation efficiency of RhB in visible light. In their study, 25 mg of Ag_2 CO_3/AC was dispersed in 100 ml of RhB solution of 10 mgl^{-1}. After 140 min of visible light exposure about 96.6 % of RhB degraded. It has been reported that the degradation rate of 10.22 times Ag_2 CO_3/AC composite is higher than the pure

$Ag_2 CO_3$ [45].

Jiang et al., (2015) showed the enhanced photo activity of $CaIn_2S_4$/g-C_3N_4 composite catalysts toward the methyl orange degradation under visible light radiation. In their findings the degradation rate of MO over the pure gC_3N_4 and $CaIn_2S_4$ were only 10% and 65% under directly visible light exposures for 120 min but $CaIn_2S_4$/g-C_3N_4 photocatalysts showed the best MO photodegradation efficiency of 90% under 120 min irradiation. g-C_3N_4 over $CaIn_2S_4$ have less e^- - h^+ recombination rates [46].

Li et al., (2016) studied the photo-assisted degradation of methylene blue using g-C_3N_4/TiO_2 hybrid photocatalysts prepared via modified sol-gel technique. In comparison with pure TiO_2 and g-C_3N_4, the synthesized g-C_3N_4/TiO_2 sample showed the maximum photocatalytic action in visible light irradiation. The enhancement in photocatalytic performance of g-C_3N_4/TiO_2 nanocomposite semiconductor was due to the high adsorption and lesser recombination of photo generated electron-hole pair. 0.1g of photocatalyst dispersed in 100 ml of methylene blue (0.01 g L^-1) and completely degraded MB within 360 min irradiation [47].

Khataee et al., (2017) carried out the photodegradation of RB 69 using TiO_2-Biochar prepared by sol-gel method under UV light. In comparison with pure biochar and TiO_2, the hybrid catalysts showed higher photocatalytic activity under both UV light irradiation. At pH 7, 1.5 g/L of TiO_2-BC composites achieved 97.5% RB 69 degradation after 80 min of UV light irradiation [48].

Yuan et al., (2017) successfully prepared C_3N_4/ZnAl-LDH nanocomposite via situ crystallization method and studied the increased photocatalytic performance by loading C_3N_4 over ZnAl-LDH [49].

Ma et al., (2015) explored the purification of contaminated water with use of Ag--$CoFe_2O_4$-GO. In their studies, nanocomposite was fabricated to disinfect both bacteria and Pb(II) present in contaminated water [50].

Justification of the research topic

This topic has been chosen by taking inspiration from recent studies which shows the promising results for hetero-structured semiconductors. The hetero-structured semiconductors have suitable band gap, high charge mobility and minimum electrons-holes recombination and high absorption coefficient, these properties makes these nanocomposites highly useful. Most important application of these nanocomposites lies in photocatalysis. In a race of designing a future material, we have chosen Bismuth-based hetero-structured nanocomposites for study and exploration.

Objectives

Due to extensive application of hetero-structured semiconductor in photocatalysis for waste water remediation the current research work will be proposed with the objectives listed below.

1. To synthesize binary and ternary hetero-structured photocatalysts comprising n & p type semiconductors.
2. Exploration of natural pigments such as Chlorophyll, lycopene, carotenes etc. for the enrichment of photocatalytic properties of as synthesized photocatalysts.
3. To characterize the synthesized nanomaterials by the techniques as Fourier Transform Infrared spectroscopy (FTIR), Transmission Electron Microscopy (TEM), Small Area Electron Diffraction (SAED), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDX),Vibrating Sample Magnetometer (VSM), Photoluminescence (PL), X-Ray Photoelectron Spectroscopy (XPS) etc.
4. To study the band gap parameters and optical properties of as synthesized photocatalyst.
5. To operate the synthesized photocatalyst for the degradation of organic and inorganic toxins from the simulated wastewater via simultaneous photocatalysis and adsorption.

Research Methodology:

Chlorophyll extraction

Chlorophyll will be extracted from fresh green leaves. The leaves will be washed by using de-ionized water and cut into small pieces. Afterwards, the sliced leaves will be dried at 60^{o}C for 2h. The sliced mass will be mixed with absolute ethanol. The ethanoic mass of the leaves will be filtered and the filtrate will be kept at -4^{o}C for further use [51].

Reduced graphene oxide preparation

Porous RGO will be synthesized by reducing exfoliated porous GO using hydrazine as reducing agent. About, 3 ml of hydrazine hydrate will be added drop-wise into the porous graphene oxide dispersion and the mixture will be stirred at 95^{o}C for 1 h. The product will be washed by using ethanol and distilled water for several times and dried out at room temperature for 12 hrs to obtain reduced graphene oxide [52].

Synthesis of Chlorophyll sensitized hetero-junctions $(BiO)_2CO_3/CdWO_4$/RGO nanocomposite

A two-step route will be used to synthesized chlorophyll modified hetero-junctions $(BiO)_2CO_3/CdWO_4$/RGO nanocomposite. In first step, nanocomposite will be fabricated via in situ co-precipitating method. The RGO (200 mg) will be homogeneously dispersed in 100 mL deionized water by sonication. Afterwards, 0.5 g $(BiO)_2CO_3$ and 1.5g $CdCl_2$ will be added into the above prepared suspension with constant stirring. Than 0.1 N solution of Na_2WO_4 will be added gradually to the resulted suspension. After vigorously stirring for 2 hrs, the resultant precipitate will be washed by using ethanol and de-ionised water to remove any residual alkaline species and then dried at 60^{o}C for 24 hrs. The second step involve the modification of $(BiO)_2CO_3/CdWO_4$/RGO with chlorophyll. A certain quantity of $(BiO)_2CO_3/CdWO_4$/RGO composite will be put in a watch glass which contained previously extracted chlorophyll solution. The contents will be left overnight without disturbing. Finally, the composite will be washed with water and ethanol mixture to remove the excess of chlorophyll [53, 54].

Optical Band Gap /Band structure Studies:

For computation of optical band gap, a suspension of 5 mg nanoparticles will be prepared in ethanol. Afterwards, the suspension will be then ultrasonicated for 30 minutes. The UV-vis. spectrum will be recorded via double-beam spectrophotometer. The band gap of the composite will be calculated by using Tauc relation:

$$\alpha h\nu = B(h\nu - E_g)^n$$

α is absorption coefficient (2.303A/l), hν the photon energy, B the band tailing parameter, Eg is the band gap and n = 1/2 for direct band gap semiconductors.

The optical band gap will be determined by extrapolating the straight line to portion of the curve between $(\alpha h\nu)^2$ and hν when α = 0.

The energy band of nanoparticles will be calculated using following relation:

$$E_{VB} = X - E^e + 0.5E_g$$
$$E_{CB} = E_{VB} - E_g$$

Where E_{VB} and E_{CB} are the band edge potentials of valence band and conduction band respectively, E^e is the energy of the free electrons on hydrogen scale (~4.5 eV), X is the geometric mean of the absolute electronegativity of the constituent atoms on Pearson scale (PAE) and E_g is the band gap energy of semiconductor in electron volts.

Characterization techniques:

The X-ray diffraction (XRD)

XRD studies is used to find the lattice parameters and crystal structure. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. X-rays are produced through a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. Scherer's formula has been used for determination of crystallite size as:

$$P = \frac{K\lambda}{\beta \cos\theta}$$

Where P is the crystallite size, and β the full width at half-maximum;

K = 0.9 and λ = 1.54 Å for Cu Kα radiation.

The d-spacing has been calculated using Bragg's diffraction law

$n\lambda = 2d \sin\theta$

X-ray photoelectron spectroscopy (XPS)

XPS is a quantitative spectroscopic technique used for the surface characterization. XPS spectra has been attained by irradiating a beam of X-rays on material and simultaneously determining the kinetic energy and number of electrons that escape from the material being analysed. It is used to measure the elemental composition, chemical state and electronic state of the elements within a material. The kinetic energy is given as:

$$E_k = h\nu - E_B$$

where E_B is the electron binding energy, is the electron kinetic energy, measured by the instrument, and hv is the photon energy (h is Planck's constant and v is the X-ray frequency).

Scanning electron microscope (SEM)

SEM is a type of electron microscope that produces high-resolution imaging of the samples by scanning the surface with high-energy beam of electrons. The electrons hit the surface atoms of sample and reflected to producing the signals which provides the information about the surface topography and composition. SEM has superior resolution as compared to light microscope because wavelength of electrons is much smaller than the wavelength of light.

Transmission Electron Microscope (TEM)

TEM is an electron microscope that uses an electron beam to pass through the specimen and an image is formed on fluorescent screen or to be detected by a sensor. The images of the TEM provide compositional, crystalline and morphological information.

Fourier transfer infra- red spectroscopy (FTIR)

FTIR spectroscopy is a technique used for identifying and analysing chemical compounds. An infrared radiations are bombarded on the sample and the amplitude of the wavelength increases when frequency of the IR radiations matches with the frequency of the bond and absorbed. The infrared absorption bands tells about the types of molecular components.

Vibrating sample magnetometer (VSM)

VSM is an instrument which measure the magnetic properties of the material. VSM technique based on Faraday's Law of Induction, according to which changing magnetic field will produce an electric field and gives the information about the changing magnetic field.

Applications

a) **Photo-assisted degradation of various pollutants such as pharmaceutical effluents, phenols etc.**

   The photocatalytic activity of synthesized nanocomposite will be studied using removal of organic contaminants under sunlight. In this, a known quantity of nanocomposite (typically 50mg-100mg) will be added to the aqueous solution of pollutants (10-5 M for dyes, 30-50 ppm for phenols etc.).The reaction vessel will be kept in dark for adsorption desorption

equilibrium then solution will be kept in sunlight for degradation. The absorbance will be recorded as the function of decrease of concentration at different interval of times using double beam UV-Visible spectrophotometer. The removal and mineralization of pollutants will also be determined using GC-MS analysis, chemical oxygen demand (COD) removal, total organic carbon (TOC) removal and CO_2 emission.

The % age degradation of pollutants will be analyzed by using the formula:

$$\frac{C_0 - C_t}{C_o} \times 100$$

where C_0 = initial concentration of pollutant

C_t = concentration of pollutant after time t.

For analyzing the photo activity of the composite, we need to study the effect of adsorption on pollutants removal. The rate of photocatalytic degradation depends on concentration of pollutant in solution as well as on the surface of the catalyst. The total pollutant concentration at any time is

$$C = C_b + C_s$$

where C_b and C_s are the amount of dye in bulk and on the surface, respectively. The quantity of dye adsorbed on the catalyst surface is calculated as

$$C_s = (C_0 - C_e)\frac{V}{M}$$

where V is the volume of solution and M is the mass of the adsorbent.

b) Photo-oxidation/reduction of carcinogenic metals such as As, Cr etc.

The photocatalytic activities of the synthesized catalysts for As(III) and Cr(VI) photo-reduction/oxidation will be investigated. As(III) and Cr(VI) photo-reduction/oxidation will be carried out in a photo-reactor equipped with a 500 ml thermostated cylindrical Pyrex vessel irradiated directly by a high pressure halogen lamp (500 W). About, 0.5 g of the photo-catalyst will be diluted in 500 ml of 50 mg/l As(III) and Cr(VI) solution. The suspension will be kept in the dark for 120 min to obtain the adsorption equilibrium and then the reduction/oxidation experiment will be tested out. During the photo-reaction, samples will be collected at regular time intervals. The photo-catalyst will be removed by filtration and then As(III) and Cr(VI) concentration will be determined by UV–vis spectrophotometer.

Major equipment and lab facilities required

The major equipment's required for this research work are Scanning electron microscope (SEM), Transmission electron microscope (TEM), X-ray diffractrometer (XRD), Fourier transform infrared (FTIR) spectroscopy, X-Ray Photoelectron Spectroscopy (XPS), Energy-dispersive X-ray (EDX) spectroscopy, muffle furnace, magnetic stirrer and UV-visible spectrophotometer etc. All the basic lab facilities and some instruments such as muffle furnace, UV-vis spectrophotometer etc. are available in IEC University. The other instrumental will be availed from IIT Mandi, IIT Ropar, IIT Roorkee and SAIF lab Punjab University.

Thesis outline

Chapter 1: Introduction

Chapter 1 **"Introduction"** includes basic introduction, history, nature, properties and various applications of nanocomposites.

Chapter 2: Literature Review

Chapter 2 **"Literature Review"** describes development and literature of concerned previous results on the Bismuth-based nanocomposites.

Chapter 3: Experimental techniques

Chapter 3 **"Experimental Techniques"** gives a brief description of synthesis techniques as well as the instrumentation of charaterization techniques which have been used in the present work. **Chapter 4:** Results and Discussion

Chapter 4 **"Results and discussion"** presents describes the studied experimental results of structural, micro- structural, optical, and magnetic properties of prepared nanocomposites. The degradation of dyes and electrochemical sensing will be part of chapter.

Chapter 5: Summary and Conclusion

Chapter 5 **"Summary and Conclusion"** summarizes our research work in brief and presents the major conclusions drawn from the research work.

Chapter 6: Scope of Future Work/Future Prospective

Chapter 6 **"Scope of Future Work"** includes the major suggestions for the future scope of work in this area of research.

Chapter 7: References.

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